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Greenhouse crop residues: Energy potential and models for the prediction of their higher heating value

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ABSTRACT

Almería, in southeastern Spain, generates some 1,086,261 t year^{-1} (fresh weight) of greenhouse crop (*Cucurbita pepo* L., *Cucumis sativus* L., *Solanum melongena* L., *Solanum lycopersicum* L., *Phaseoulus vulgaris* L., *Capsicum annuum* L., *Citrillus vulgaris* Schrad. and *Cucumis melo* L.) residues. The energy potential of this biomass is unclear. The aim of the present work was to accurately quantify this variable, differentiating between crop species while taking into consideration the area they each occupy. This, however, required the direct analysis of the higher heating value (HHV) of these residues, involving very expensive and therefore not commonly available equipment. Thus, a further aim was to develop models for predicting the HHV of these residues, taking into account variables measured by elemental and/or proximate analysis, thus providing an economically attractive alternative to direct analysis. All the analyses in this work involved the use of worldwide-recognised standards and methods. The total energy potential for these plant residues, as determined by direct analysis, was 1,003,497.49 MW h year^{-1}. Twenty univariate and multivariate equations were developed to predict the HHV. The R^2 and adjusted R^2 values obtained for the univariate and multivariate models were 0.909 and 0.946 or above respectively. In all cases, the mean absolute percentage error varied between 0.344 and 2.533. These results show that any of these 20 equations could be used to accurately predict the HHV of crop residues. The residues produced by the Almería greenhouse industry would appear to be an interesting source of renewable energy.

Contents

1. Introduction

Greenhouses and macrotunnels occupy some 1.6×10^6 ha worldwide. The Far East accounts for some 80% of this figure [1]; the other main area is the Mediterranean with some 0.19×10^6 ha. Italy accounts for some 67,700 ha and Spain some 55,800 ha [2]. Seventy percent of Spain's greenhouses are found in the country's southeast, in the Provinces of Almería, Granada and Murcia [3]. Among these, the Province of Almería is the most important with some 25,902 ha of greenhouses [4] largely given over to the production of tomatoes, peppers, melons, water melons, aubergines, courgettes, cucumbers and beans; a small number of hectares are devoted to the production of lettuce and ornamental plants [5]. After harvest, some 769,500 t year^{-1} (fresh weight) of crop residues remain (assuming an area occupied by greenhouses of 27,000 ha) [6,7].

The use of plant biomass as a fuel is environmental friendly since only the CO_2 taken up by the plants during their growth is returned to the atmosphere during combustion (i.e., it is a

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Table 1
Crop residue biomass produced by the greenhouse agriculture industry in Almería.

Studied species	Plant remains ($t\,ha^{-1}\,year^{-1}$) [21,22]	Area occupied 07/08 (ha) [23]	Biomass ($t\,year^{-1}$) fresh weight	Biomass ($t\,year^{-1}$) dry weight
Cucurbita pepo L.	20	4492	89840	17968
Cucumis sativus L.	24	4551	109224	21844.8
Solanum melongena L.	27	1622	43794	8758.8
Solanum lycopersicum L.	49	10250	502250	100450
Phaseoulus vulgaris L.	23	1259	28957	5791.4
Capsicum annuum L.	28	7057	197596	39519.2
Citrillus vulgaris Schrad.	24	4775	114600	22920
Cucumis melo L.	33	4981	164373	32874.6
Total	228	38987[a]	1086261	250126.8

[a] This differs from that reported by Sanjuán [4] since some 50% of all greenhouses produced two crops per year [24].

carbon-neutral process) [8]. Moreover, plant biomass represents a renewable resource of energy. Assessing the energy potential of these residues is therefore important. Recent studies in this line have been undertaken in China [9,10], Malaysia (involving banana) [11], the Argentine Pampa (involving soy) [12], and in rural areas of Turkey where such remains are already being used as a fuel [13]. The ashes formed in the combustion process also have their uses, e.g., as fertilizers or for making cement [14]. Unfortunately, the inorganic components of biomass can cause pollution problems during burning, and K, Na, S, P, Ca, Mg, Fe, and in particular Cl, have all been implicated in the deterioration of furnaces [15]. Biomass also has limitations as an energy source given its variable physical properties and in terms of supply [16]. Nevertheless, it is recognised as one of the most important sources of renewable energy for the near future [17].

The use of biomass requires that its higher heating value (HHV) be known, but the equipment required renders the direct analysis of this costly. A number of mathematical models have therefore been proposed to determine the HHV from proximate analysis, elemental analysis and chemical composition analysis [18–20]. Callejón-Ferre and López-Martínez [6] described the HHV of greenhouse crops in Almería to lie between 15,073.2 $kJ\,kg^{-1}$ and 15,491.9 $kJ\,kg^{-1}$, although this work involved samples of bricks produced from plant remains without taking into account the species involved. If a mean HHV of 15,282.55 $kJ\,kg^{-1}$ is assumed, while understanding fresh residue to contain at least 80% water [21], and taking into account the dry biomass generated per year (250,126.8 $t\,year^{-1}$) (Table 1), the mean energy potential of the greenhouse crop residues (without taking species into account) produced in Almería is 3822,575,327.34 $MJ\,year^{-1}$ or 1,061,826.48 $MW\,h\,year^{-1}$.

The aim of this work was: (1) to determine, via direct analysis, the HHV, and therefore the energy potential, of the greenhouse crop residues produced in Almería, differentiating between plant species while taking into account the area they each occupy, and (2) to develop models for predicting the HHV of these species taking into account variables measured by elemental and/or proximate analysis, thus providing an economically attractive alternative to direct analysis.

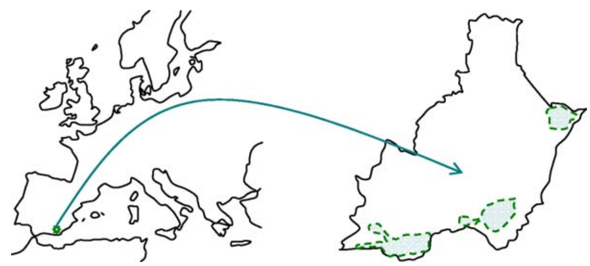


Fig. 1. Location 80% of the greenhouses in Almería [25].

2. Material and methods

The crop species taken into account in this work were courgette (*Cucurbita pepo* L.), pepper (*Cucumis sativus* L.), aubergine (*Solanum melongena* L.), tomato (*Solanum lycopersicum* L.), bean (*Phaseoulus vulgaris* L.), pepper (*Capsicum annuum* L.), water melon (*Citrillus vulgaris* Schrad.) and melon (*Cucumis melo* L.). These species represent nearly 100% of all the crops grown in Almería's greenhouses (Fig. 1).

2.1. Samples for the direct analysis of HHV, element analysis, proximate analysis, and the determination of ash element content and ash fusibility

Two plants of each species were randomly selected a little before the end of their lives. All plant samples were taken to the laboratory within 24 h, where the aerial parts were separated from the roots and any other auxiliary elements (raffia, plastic, etc.) (Fig. 2).

Table 2 shows the variables examined and the analysis standards followed. All analyses were undertaken at the *Escuela Superior de Ingenieros de Sevilla*.

All analyses of all variables were performed in quintuplicate for each species (more than the figure required by the standards outlined in Table 2), except for humidity, fixed carbon, chlorine, metals and ash fusibility, for which the numbers of repetitions required by each method were adhered to. The aim of performing five analyses per species was to increase the sample size available for univariate and multivariate regression analysis of the results



Fig. 2. Left: remains of cucumber plants with auxiliary elements (roots, plastic). Right: tomato remains with these auxiliary elements removed, ready for analysis.

Table 2
Biomass analysis methods.

Property	Analytical method
Proximate analysis	
Moisture content	UNE-CEN/TS 14780:2008 EX [26]
	UNE-CEN/TS 14774-1:2007 EX [27]
Ash	UNE-CEN/TS 14775:2007 EX [28]
Volatile compounds	UNE-CEN/TS 15148:2008 EX [29]
Fixed carbon	By subtraction
Elemental analysis	
Carbon (C)	UNE-CEN/TS 15104:2008 EX [30]
Hydrogen (H)	UNE-CEN/TS 15104:2008 EX [30]
Nitrogen (N)	UNE-CEN/TS 15104:2008 EX [30]
Sulphur (S)	ASTM D4239-08 [31]
Oxygen (O)	By subtraction
Chlorine (Cl)	ASTM E776-87 [32]
Higher heating value via direct analysis	UNE 164001:2005 EX [33]
Ash elemental (metals)	UNE-CEN/TS 14775 EX [28]
Ash fusibility	ASTM D1857-04 (oxidising atmosphere) [34]

obtained by proximate and elemental analysis. Fixed carbon was not determined in proximate analysis nor was oxygen determined in elemental analysis since these variables can be calculated by subtraction (see Table 2).

2.2. Predictive equations

A maximum of six variables, determined by elemental and/or proximate analysis, were taken into account in each equation for predicting the HHV. The reliability of the equations was tested by determining, with respect to the direct analysis method, the coefficient of regression (R^2) (univariate models), the adjusted R^2 (multivariate models), the mean square of errors (MSE), the root mean square of errors (RMSE), the mean absolute percentage error (MAPE), and Akaike's Information Criterion (IC) and Schwarz's Bayesian Criterion (BC) values [35–37]. All calculations were performed using XLSTAT 2009 software.

3. Results

Table 3 shows the results obtained by proximate analysis, elemental analysis and the direct analysis of HHV. Proximate analysis showed the moisture content of all the species analysed to surpass 80%; the species with the smallest moisture content was *C. annuum* L. (80.91%) and that with the largest was *C. pepo* L. (93.04%). The fixed carbon content varied from 8.24% in *C. pepo* L. to 15.99% in *S. melongena* L. The highest ash value was obtained for *C. pepo* L. (29.75%) while the smallest was recorded for *S. melongena* L. (13.12%). Volatile compound values ranged from 61.68% in *C. sativus* L. to 71.67% in *P. vulgaris* L.

Elemental analysis showed the carbon content to range from 33.81% in *C. sativus* L. to 42.86% in *P. vulgaris* L., hydrogen from 3.70% in *C. pepo* L. to 4.81% in *P. vulgaris* L., nitrogen from 2.18% in *S. melongena* L. to 4.70% in *C. pepo* L., sulphur from 0.10% in *S. melongena* L. to 0.50% in *S. lycopersicum* L., oxygen from 27.84% in *C. pepo* L. to 37.95% in *S. melongena* L., and chlorine from 7838 ppm in *C. annuum* L. to 29,362 ppm in *S. lycopersicum* L.

The direct analysis of HHV returned the highest value for *P. vulgaris* L., with 17,014.23 kJ kg^{-1}, and the smallest value for *C. sativus* L., with 12,595.82 kJ kg^{-1}.

The ash aluminium content was highest in *S. lycopersicum* L. at 6.67 mg kg^{-1} and lowest in *C. annuum* L. at 1.15 mg kg^{-1} (Table 4). Ash calcium ranged from 147.72 mg kg^{-1} in *C. pepo* L. to 293.48 mg kg^{-1} in *C. vulgaris* Schrad., ash copper from 1.94 mg kg^{-1} in *C. annuum* L. to 727.00 mg kg^{-1} in *C. sativus* L., ash iron from 1.18 mg kg^{-1} in *C. annuum* L. to 799 mg kg^{-1} in *C. vulgaris* Schrad., ash potassium from 52.89 mg kg^{-1} in *C. pepo* L. to 165.22 mg kg^{-1}

Table 3
Results of proximate analysis, elemental analysis, and direct analysis of HHV for each species.

Species	Proximate analysis				Elemental analysis						Direct analysis of HHV
	W	FC	A	V	C	H	N	S	O	Cl	
Cucurbita pepo L.	93.04	8.24 ± 0.16	29.75 ± 0.09	62.01 ± 0.09	33.88 ± 0.50	3.70 ± 0.08	4.70 ± 0.07	0.13 ± 0.02	27.84 ± 0.66	10762	12849.37 ± 0.04
Cucumis sativus L.	89.36	10.35 ± 0.18	27.96 ± 0.13	61.68 ± 0.09	33.81 ± 0.27	3.87 ± 0.15	3.00 ± 0.02	0.24 ± 0.02	31.12 ± 0.47	11063	12595.82 ± 0.05
Solanum melongena L.	83.64	15.99 ± 0.19	13.12 ± 0.22	70.89 ± 0.10	42.09 ± 0.12	4.56 ± 0.18	2.18 ± 0.07	0.10 ± 0.01	37.95 ± 0.30	9970	16529.71 ± 0.03
Solanum lycopersicum L.	89.54	15.27 ± 0.15	18.71 ± 0.18	66.02 ± 0.10	38.17 ± 0.10	4.08 ± 0.08	2.30 ± 0.07	0.50 ± 0.02	36.24 ± 0.30	29362	14826.78 ± 0.05
Phaseolus vulgaris L.	85.52	12.92 ± 0.18	15.41 ± 0.12	71.67 ± 0.06	42.86 ± 0.35	4.81 ± 0.05	3.62 ± 0.08	0.12 ± 0.01	33.18 ± 0.48	14503	17014.23 ± 0.04
Capsicum annuum L.	80.91	12.64 ± 0.56	17.86 ± 0.49	69.50 ± 0.11	39.27 ± 0.04	4.17 ± 0.04	3.28 ± 0.02	0.40 ± 0.04	35.01 ± 0.52	7838	15264.44 ± 0.06
Citrillus vulgaris Schrad.	90.84	12.58 ± 0.31	20.58 ± 0.30	66.84 ± 0.09	37.64 ± 0.25	4.62 ± 0.04	3.60 ± 0.05	0.15 ± 0.01	33.41 ± 0.32	10380	14258.58 ± 0.05
Cucumis melo L.	91.85	10.37 ± 0.23	24.38 ± 0.13	65.25 ± 0.18	35.50 ± 0.15	4.37 ± 0.11	4.62 ± 0.06	0.17 ± 0.03	30.96 ± 0.28	9793	13501.26 ± 0.05

M: total moisture content (%); FC: fixed carbon (% dry weight); A: ash (% dry weight); V: volatile compounds (% dry weight); C: carbon (% dry weight); H: hydrogen (% dry weight); N: nitrogen (% dry weight); S: sulphur (% dry weight); O: oxygen (% dry weight); Cl: chlorine (ppm) and HHV: higher heating value (kJ kg^{-1} dry weight).

Table 4
Ash metal contents of the studied species.

Species	Ash metals (mg kg^{-1})											
	Al	Ca	Cu	Fe	K	Mg	Mn	Mo	Na	P	Si	Ti
Cucurbita pepo L.	2.79	147.72	54.00	1.99	52.89	39.96	153.00	6.00	3.34	35.73	22.41	157.00
Cucumis sativus L.	2.00	210.55	727.00	766.00	62.19	87.29	2.69	18.00	32.36	24.68	27.41	80.00
Solanum melongena L.	4.76	199.65	97.00	3.28	162.81	25.06	112.00	1.00	13.86	11.04	34.62	270.00
Solanum lycopersicum L.	6.67	176.87	2.09	6.81	107.65	47.72	456.00	1.00	40.90	10.94	47.69	1.54
Phaseoulus vulgaris L.	2.63	153.70	625.00	2.21	55.27	38.54	590.00	12.00	5.08	29.16	42.00	179.00
Capsicum annuum L.	1.15	186.64	1.94	1.18	165.22	18.58	202.00	2.00	13.22	18.11	30.99	99.00
Citrillus vulgaris Schrad.	1.36	293.48	62.00	799.00	111.25	53.36	374.00	3.00	9.25	40.14	20.96	255.00
Cucumis melo L.	1.87	210.58	61.00	718.00	151.15	47.18	363.00	6.00	36.90	24.23	16.13	222.00

Table 5
Ash fusibility of the studied species.

Species	Fusibility			
	IT (°C)	ST (°C)	HT (°C)	FT (°C)
Cucurbita pepo L.	1546.00	1553.00	1650.00	1650.00
Cucumis sativus L.	993.00	1650.00	1650.00	1650.00
Solanum melongena L.	1650.00	1650.00	1650.00	1650.00
Solanum lycopersicum L.	994.00	1650.00	1650.00	1650.00
Phaseoulus vulgaris L.	1353.00	1650.00	1650.00	1650.00
Capsicum annuum L.	993.00	1650.00	1650.00	1650.00
Citrillus vulgaris Schrad.	No data	No data	No data	No data
Cucumis melo L.	No data	No data	No data	No data

IT: deformation temperature; ST: softening temperature; HT: hemisphere temperature; FT: fluidity temperature.

in *C. annuum* L., ash magnesium from 18.58 mg kg^{-1} in *C. annuum* L. to 87.29 mg kg^{-1} in *C. sativus* L., ash manganese from 2.69 mg kg^{-1} in *C. sativus* L. to 590.00 mg kg^{-1} in *P. vulgaris* L., ash molybdenum from 1.00 mg kg^{-1} in *S. melongena* L. and *S. lycopersicum* L. to 18.00 mg kg^{-1} in *C. sativus* L., ash sodium from 3.34 mg kg^{-1} in *C. pepo* L. to 40.90 mg kg^{-1} in *S. lycopersicum* L., ash phosphorus from 10.94 mg kg^{-1} in *S. lycopersicum* L. to 40.14 in *C. vulgaris* Schrad., ash silicon from 16.13 mg kg^{-1} in *C. melo* L. to 47.69 in *S. lycopersicum* L., and ash titanium from 1.54 mg kg^{-1} in *S. lycopersicum* L. to 270.00 mg kg^{-1} in *S. melongena* L.

Table 5 shows the ash fusibility values recorded. All species showed the same value of 1650 °C for all variables except for the deformation temperature (IT), which ranged from 993 °C in *C. annuum* L. and *C. sativus* L. to 1650 °C in *S. melongena* L., and for the softening temperature, which was 1533 °C for *C. pepo* L. alone. No data are available for *C. melo* L. or *C. vulgaris* Schrad. owing to the breakdown of the necessary apparatus.

Table 6 shows the energy potential of the biomass residue by species and as a total. These figures were obtained from the HHV values in Table 3 and the biomass values in Table 1.

P. vulgaris L. returned the highest value at 4.73 kW h kg^{-1}, while *C. sativus* L. returned the smallest, with 3.50 kW h kg^{-1}. When the number of tonnes of remains produced per year for each species is taken into account, *S. lycopersicum* L. returns the highest value at 413,708.35 MW h year^{-1} while *P. vulgaris* L. returns the lowest at 27,371.17 MW h year^{-1}.

Fifty mathematical equations were tested for the prediction of HHV in MJ kg^{-1} from the results returned in the proximate and elemental analyses (Table 7), of which 20 were finally selected as providing an adequate result.

Among the selected equations, or predictive models (Table 8, Fig. 3), some were linear and others quadratic, and took into account from one to six variables from among the following: [A], [V], [C], [H], [N], [S], [C + N], [H + N], [A + N], [C + S], [V + N], [A^2H], [V^2H], [C^2N], [H^2A], [S^2A], [S^2N], [C^2], [A^2], [N^2], [H^{-1}] and [V^{-1}].

In comparison with the HHV results obtained by direct analysis, all the selected equations showed an R^2 or an adjusted R^2 of ≥0.909. The median R^2 for the univariate models was 0.963 while that of the adjusted R^2 for the multivariate models was 0.990. The minimum and maximum R^2 values obtained for the univariate models were 0.909 (equation 1) and 0.990 (equations 4 and 13) respectively. For the multivariate models, the minimum and maximum adjusted R^2 values were 0.946 (equation 3) and 0.997 (equation 19) respectively.

The MSE ranged from 0.001 (equation 20) to 0.222 (equation 1); the median MSE was 0.021 and the mean 0.04. The RMSE ranged from 0.068 (equation 19) to 0.471 (equation 1); the median RMSE was 0.146 and the mean 0.175. The minimum MAPE was 0.344 (equation 19) and the maximum 2.533 (equation 1); the median MAPE was 0.708 and the mean 0.905. Akaike's IC value ranged from −209.264 (equation 19) to −58.211 (equation 1); the median Akaike's IC was −149.969 and the mean −145.071. Finally, the

Table 6
Energy potential of the studied greenhouse crops.

Species	Biomass (t year^{-1})	HHV (kJ kg^{-1})	kW h kg^{-1}	MJ year^{-1}	MW h year^{-1}
Cucurbita pepo L.	17968.0	12849.37	3.57	230877.48	64132.63
Cucumis sativus L.	21844.8	12595.82	3.50	275153.17	76431.44
Solanum melongena L.	8758.8	16529.71	4.59	144780.42	40216.78
Solanum lycopersicum L.	100450.0	14826.78	4.12	1489350.05	413708.35
Phaseoulus vulgaris L.	5791.4	17014.23	4.73	98536.21	27371.17
Capsicum annuum L.	39519.2	15264.44	4.24	603238.46	167566.24
Citrillus vulgaris Schrad.	22920.0	14258.58	3.96	326806.65	90779.63
Cucumis melo L.	32874.6	13501.26	3.75	443848.52	123291.26
Total				3612590968.31	1003497.49

HHV: higher heating value.

Table 7
Data replicates for the regression models.

Species	Proximate analysis		Elemental analysis				Direct analysis of HHV
	A	V	C	H	N	S	
Cucurbita pepo L.	29.83	61.95	34.28	3.64	4.74	0.14	12.85
	29.63	61.95	33.05	3.59	4.57	0.17	12.88
	29.70	61.93	34.25	3.77	4.73	0.13	12.90
	29.79	62.11	33.87	3.74	4.75	0.11	12.82
	29.82	62.11	33.95	3.75	4.71	0.11	12.79
Cucumis sativus L.	27.93	61.67	33.84	4.05	3.00	0.25	12.54
	27.84	61.76	33.78	3.78	2.97	0.23	12.61
	27.89	61.55	33.40	3.69	3.02	0.22	12.60
	27.99	61.65	34.16	3.98	3.03	0.22	12.56
	28.17	61.77	33.86	3.85	3.00	0.26	12.67
Solanum melongena L.	13.05	70.83	42.29	4.46	2.22	0.11	16.52
	12.78	70.96	42.11	4.33	2.27	0.11	16.53
	13.34	70.74	42.01	4.82	2.11	0.11	16.48
	13.12	70.97	42.01	4.61	2.10	0.10	16.55
	13.30	70.93	42.01	4.60	2.18	0.09	16.56
Solanum lycopersicum L.	18.92	65.91	38.29	3.99	2.26	0.52	14.87
	18.66	65.91	38.09	4.04	2.29	0.52	14.86
	18.47	66.10	38.06	4.03	2.32	0.48	14.79
	18.84	66.04	38.20	4.17	2.41	0.48	14.85
	18.66	66.13	38.23	4.15	2.24	0.49	14.76
Phaseoulus vulgaris L.	15.44	71.69	43.25	4.77	3.72	0.13	17.02
	15.54	71.75	42.95	4.79	3.66	0.11	17.01
	15.30	71.62	42.29	4.88	3.59	0.12	16.95
	15.27	71.60	42.83	4.76	3.50	0.11	17.07
	15.50	71.71	42.99	4.85	3.64	0.12	17.02
Capsicum annuum L.	18.12	69.38	39.24	4.23	3.28	0.37	15.25
	17.34	69.38	39.30	4.12	3.26	0.41	15.32
	17.32	69.52	39.27	4.19	3.29	0.38	15.33
	18.16	69.56	39.22	4.15	3.26	0.46	15.22
	18.37	69.64	39.31	4.17	3.31	0.40	15.20
Citrillus vulgaris Schrad.	20.68	66.84	37.92	4.60	3.59	0.14	14.26
	20.78	66.73	37.39	4.58	3.64	0.16	14.26
	20.17	66.90	37.86	4.59	3.56	0.15	14.28
	20.37	66.78	37.40	4.66	3.67	0.14	14.30
	20.88	66.96	37.64	4.67	3.56	0.14	14.18
Cucumis melo L.	24.36	65.20	35.51	4.19	4.69	0.18	13.53
	24.31	65.38	35.36	4.41	4.56	0.21	13.46
	24.54	65.05	35.74	4.47	4.59	0.18	13.51
	24.21	65.12	35.54	4.40	4.58	0.16	13.44
	24.48	65.48	35.37	4.36	4.67	0.12	13.56

A: ash (% dry weight); V: volatile compounds (% dry weight); C: carbon (% dry weight); H: hydrogen (% dry weight); N: nitrogen (% dry weight); S: sulphur (% dry weight); HHV: higher heating value (MJ kg^{-1} dry weight).

Schwarz's BC value ranged from −197.442 (equation 19) to −54.833 (equation 1); the median Schwarz's BC value was −142.971 and the mean −137.724.

Fig. 4 shows the HHV predicted by the 20 models (*X* axis) against the experimentally obtained HHV results (*Y* axis), and their error limits. In general, all the equations appear to be reliable predictors of HHV; the smaller the distance between the grey lines the better the reliability of the model.

4. Discussion

Excluding roots (with their high soil content) and auxiliary elements such as raffia or pieces of plastic guiding cane from the analytical plant material (Fig. 2) allowed more accurate results to be obtained in the different analyses. The need for such separation should also be remembered in the operation of any future energy plant based on the combustion of greenhouse plant remains; introducing soil into furnaces reduces their efficiency and would increase the amount of ash produced [15,16]. Sulphur and chlorine can also cause the deterioration of furnaces. In the present work *S. lycopersicum* L. had the highest concentrations of these elements (29,362 ppm chlorine and 0.50% sulphur) (Table 3). This is unfortunate since it is the majority species, accounting for 41.23% of the total MW h $year^{-1}$ possible (Table 6). Callejón-Ferre and López-Martínez [6] suggest plant residues could be washed and dried (using heat provided by the furnace) before being introduced into furnaces to remove soil and auxiliary elements and to reduce the chlorine and sulphur content of the material – but this would be costly. Knowing the sulphur and chlorine contents of each species (Table 3) (or of other remains) would, however, allow for mixing such that the amounts of these elements entering a furnace would be reduced via the reduction of the proportion of *S. lycopersicum* L. Mixing with *S. melongena* L. (9970 ppm of chlorine and 0.10% sulphur) or *C. melo* L. (9793 ppm chlorine and 0.17% sulphur) would reduce the amount of chlorine entering the furnace. Mixing with *C. annuum* L. (7838 ppm chlorine and 0.40% sulphur) would reduce the chlorine but not the sulphur load. It should be borne in mind, however, that not all crops are grown at the same time. For example, *C. vulgaris* Schrad. and *C. melo* L. are only cultivated in spring; their remains, therefore, could only be used during summer and thereafter.

Proximate analysis returned ash values of over 20% for *C. pepo* L., *C. sativus* L., *C. vulgaris* Schrad. and *C. melo* L. (Table 3), while those for *S. melongena* L., *S. lycopersicum* L., *C. annuum* L. and *P. vul-*

Table 8
The 20 equations selected as predictive models.

No.	Equations	MSE	RMSE	MAPE	R^2	Adjusted R^2	Akaike's IC	Schwarz's BC
1	HHV = 20.086 – 0.261[A]	0.222	0.471	2.533	0.908522	0.906115	–58.210542	–54.832783
2	HHV = –13.173 + 0.416[V]	0.151	0.388	2.336	0.937927	0.934660	–73.722006	–70.344247
3	HHV = –2.057 – 0.092[A] + 0.279[V]	0.128	0.358	2.040	0.948774	0.946005	–79.404446	–74.337808
4	HHV = –3.147 + 0.468[C]	0.027	0.163	0.793	0.989012	0.987277	–142.981620	–139.603861
5	HHV = –2.907 + 0.491[C] – 0.261[H]	0.023	0.152	0.729	0.990712	0.989205	–147.704193	–142.637554
6	HHV = –3.393 + 0.507[C] – 0.341[H] + 0.067[N]	0.021	0.146	0.719	0.991670	0.990282	–150.060034	–143.304516
7	HHV = –1.563 – 0.0251[A] + 0.475[C] – 0.385[H] + 0.102[N]	0.021	0.145	0.709	0.992040	0.990676	–149.878107	–141.433710
8	HHV = – 0.465 – 0.0342[A] – 0.019[V] + 0.483[C] – 0.388[H] + 0.124[N]	0.022	0.147	0.696	0.992077	0.990679	–148.063200	–137.929923
9	HHV = –0.603 – 0.033[A] – 0.019[V] + 0.485[C] – 0.380[H] + 0.124[N] + 0.030[S]	0.022	0.149	0.697	0.992081	0.990641	–146.081640	–134.259484
10	HHV = –3.440 + 0.517[C + N] – 0.433[H + N]	0.021	0.146	0.760	0.991475	0.990092	–151.132181	–146.065542
11	HHV = –1.642 – 0.024[A] + 0.475[C + N] – 0.376[H + N]	0.020	0.143	0.707	0.992038	0.990711	–151.868565	–145.113048
12	HHV = –0.417 – 0.012[V] – 0.035[A] + [C] + 0.518[C + N] – 0.393[H + N]	0.021	0.145	0.698	0.992076	0.990718	–150.060858	–141.616460
13	HHV = 5.736 + 0.006[C^2]	0.025	0.159	0.825	0.989642	0.986643	–145.343279	–141.965520
14	HHV = –5.290 + 0.493[C] + 5.052[H^{-1}]	0.022	0.150	0.730	0.991040	0.988376	–149.141949	–144.075311
15	HHV = 9.756 – 309.454[V^{-1}] + 6.164[H^{-1}] + 0.006[C^2]	0.019	0.138	0.705	0.992590	0.990326	–154.742689	–147.987171
16	HHV = 4.622 + 7.912[H^{-1}] – 0.001[A^2] + 0.006[C^2] + 0.018[N^2]	0.016	0.126	0.618	0.993993	0.992105	–161.136988	–152.692591
17	HHV = 23.668 – 7.032[H] – 0.002[A^2] + 0.005[C^2] + 0.771[H^2] + 0.019[N^2]	0.012	0.112	0.536	0.995420	0.993939	–169.989748	–159.856471
18	HHV = 86.191 – 2.051[A] – 1.781[C] – 237.722 [A^{-1}] + 0.030[A^2] + 0.025[C^2] + 0.026[N^2]	0.008	0.092	0.438	0.996963	0.995951	–184.423908	–172.601752
19	HHV = 8.725 + 0.0007[A^2H] + 0.0004[V^2H] + 0.0002[C^2N] – 0.014[H^2A] + 0.626[S^2A] – 3.692[S^2N]	0.005	0.068	0.344	0.998368	0.997428	–209.263821	–197.441665
20	HHV = 101.450 – 2.197[A] + 0.0282[C^2] + 0.172[A + N] – 2.156[V + N] – 230.927[C + N] + 0.029[C + S]	0.001	0.100	0.486	0.996453	0.995485	–178.208471	–166.386314

A: ash (% dry weight); V: volatile compounds (% dry weight); C: carbon (% dry weight); H: hydrogen (% dry weight); N: nitrogen (% dry weight); S: sulphur (% dry weight); HHV: higher heating value (MJ kg^{-1} dry weight); MSE: mean square of errors; RMSE: root mean square of the errors and MAPE: mean absolute percentage error. The 95% confidence level applied to all equations.

garis L. were under 19%. These differences might be a reflection of these species belonging to different families; the members of the former group belong to Cucurbitaceae while those of the latter belong to Solanaceae (except for *P. vulgaris* L. which belongs to Leguminoseae). In contrast, the members of Cucurbitaceae had smaller volatile compound contents than did those of Solanaceae and Leguminoseae. The values for fixed carbon behaved in a manner similar to those for the latter compounds.

Elemental analysis showed the members of the families Solanaceae and Leguminoseae to have larger carbon contents, while those of Cucurbitaceae were lower. The carbon value showed a direct, positive relationship with HHV [18–20].

The composition of the ash was different for each species (Table 4), in agreement with that indicated by Campbell [14]. These ashes, however, could be used in the production of cement or as

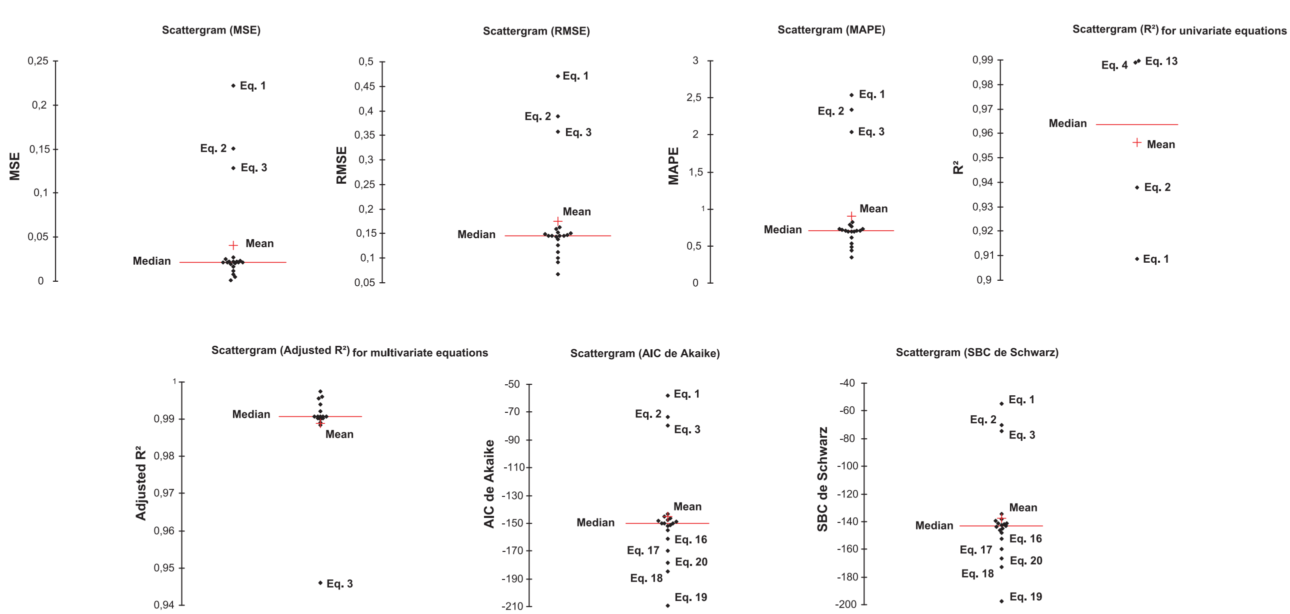


Fig. 3. Scatter graphs for the variables used in the equations (see Table 8).

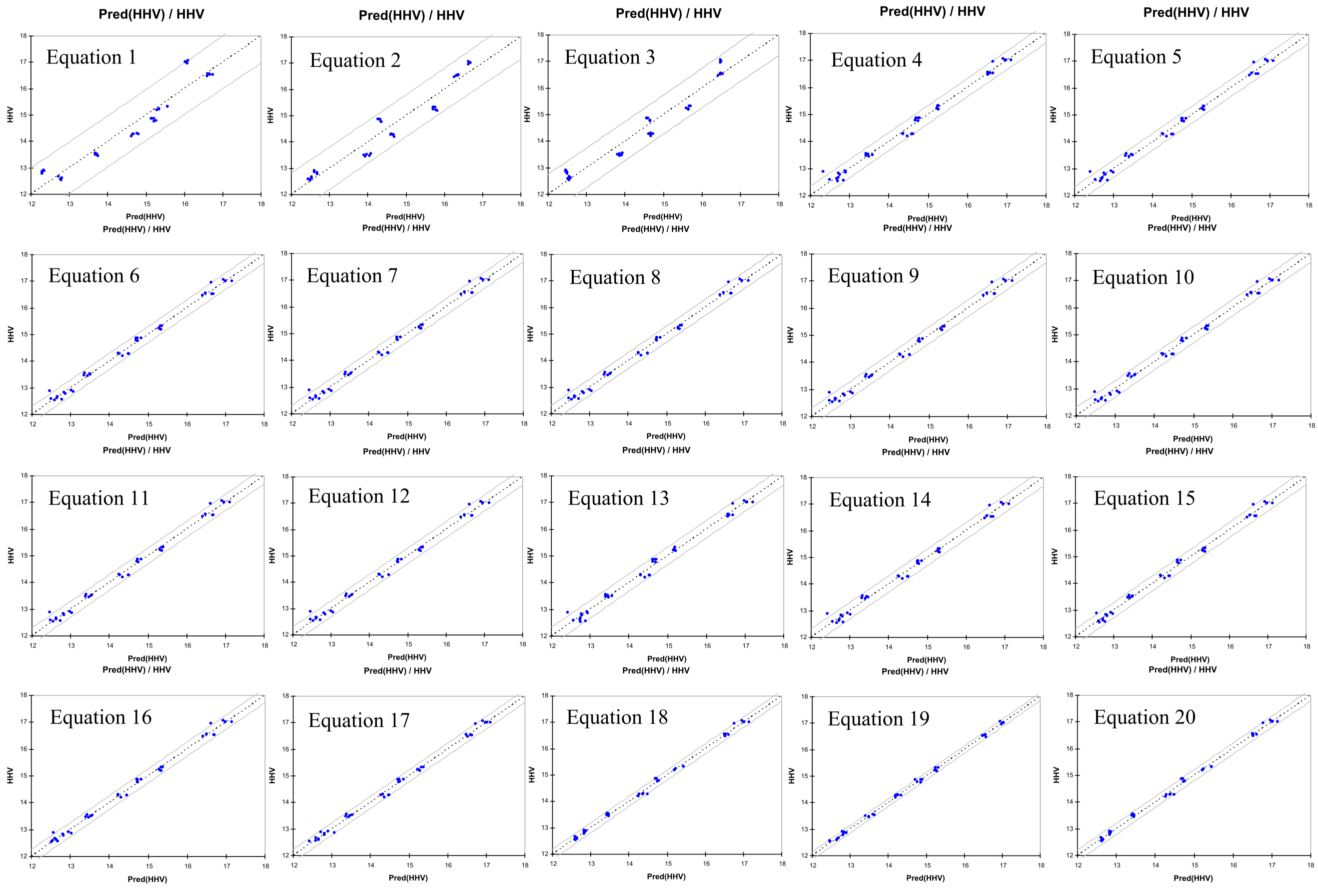


Fig. 4. Scatter graphs for the 20 equations showing their reliability as predictors of the higher heating value (Table 8).

fertilizers; their compositions suggest that such uses would not be dangerous.

The behaviour of the different species with respect to ash fusibility (Table 5) was not that expected (using the standard for coal, flying ash and slag). At some 1500 °C, the ash pyramids for all samples began to deform and at 1650 °C they disintegrated leaving no residue.

The calculated total energy potential (Table 6) was 58,328.99 MW h year^{-1} less than that described in previous work [6]. This difference is owed to the fact that the present work is more precise (given the number of repetitions) and involves separation by species.

The best model for predicting HHV would be that with the smallest number of independent variables that explains the highest percentage variation in this variable, i.e., that with the highest R^2 for univariate models or adjusted R^2 for multivariate models. Equation 19 appears to offer the best model. It has the highest adjusted R^2 and the smallest MAPE, Akaike's IC and Schwarz's BC values. However, with six variables it is not the simplest of equations to deal with, requiring as it does values provided by elemental and proximate analysis. Equations 7 (with 4 variables), 8 (with 5 variables), 9 (with 6 variables), 11 (with 4 variables), 12 (with 5 variables), 16 (with 4 variables), 17 (with 5 variables), 18 (with 3 variables – but somewhat more laborious to use), 20 (with 5 variables) suffer from the same problem. Equations 1 (with 1 variable), 2 (with 1 variable), 3 (with 2 variables), 4 (with 1 variable), 5 (with 2 variables), 6 (with 3 variables), 10 (con 3 variables), 13 (with 1 variable) and 14 (with 2 variables) are simpler and more interpretable. Among these, equation 13 appears to be the best since it has an R^2 of 0.989642. However, it has a higher MAPE (0.825%) than equation 4 (0.793%), which has an R^2 value of 0.989012. If only these criteria were of concern, the equation with the lowest error would be chosen since the R^2 values are very similar. However, the Akaike's IC and Schwarz's BC values favour equation 13 since they are smaller than those of equation 14. Thus, equation 13 might be the best choice of univariate model; in addition, it only involves variables that require elemental analysis be performed. Equation 6 (3 variables) might be the best choice of multivariate model since it has an adjusted R^2 value of 0.990282, a MAPE of 0.719%, an Akaike's IC of −150.06 and a Schwarz's BC of −143.30. Equation 10 (3 variables) has an adjusted R^2 of 0.990092, a MAPE of 0.760%, and Akaike's IC of −151.13 and a Schwarz's BC of −146.07. Thus, both equations 6 and 10 have four criteria in their favour, but equation 6 is easier to interpret since the variables are quite simple to use. The use of equation 6 would, again, only involve elemental analysis. If a model were required based only on proximate analysis, the best option would be equation 3. This involves just two variables, both of which are simple to use, has an adjusted R^2 of 0.946 and a MAPE of 2.040%. Equation 2 might also be used; this involves only one variable, has an R^2 of 0.938 and a MAPE of 2.336%.

In general all 20 selected equations predict the HHV well, and the use of none should be ruled out until the analytical equipment available – and therefore the variables that can be measured – is known.

5. Conclusions

The energy potential of the greenhouse crop remains studied was 1,003,497.97 MW h year^{-1}. The residues produced by the Almería greenhouse industry would therefore appear to be an interesting source of renewable energy. Any of these 20 equations proposed in this work could be used to accurately predict the HHV

of crop residues. The best model for predicting the HHV is provided by equation 19, even though it involves six variables. Equation 13 provides the best univariate model involving only elemental analysis (for carbon). Equation 6 provides the best multivariate model involving only elemental analysis (for carbon, hydrogen and nitrogen). Equation 3 provides the best multivariate model involving only proximate analysis (for ash and volatile compounds), and equation 2 provides the best univariate model involving only proximate analysis (for volatile compounds).

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